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CO_2 Carrying Capacities of Cement Raw Meals in Calcium Looping Systems

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ABSTRACT: Calcium looping, CaL, is an emerging CO_2 capture technology that is of special interest for use in cement plants, as it offers the possibility of exploiting several energy and material synergies. In this work, the CO_2 carrying capacity of calcined raw meal materials for cement plants has been investigated with thermogravimetric equipment in a wide range of testing conditions. When calcination was carried out at high temperatures and over long times, some raw meals display a sharp decrease in their subsequent CO_2 capture capacity compared to their limestone counterparts, while others perform as expected from their CaO content. XRD observations of calcined samples confirmed the formation of Ca_2SiO_4, i.e., belite, as the main deactivation agent, since belite formation removes active CaO for CO_2 capture during the carbonation stage. The extent of belite formation was found to be greatly influenced by the nature of the raw meal (in particular by the level of aggregation of Ca and Si atoms in the material), by the calcination temperature, by reaction atmosphere, and by the duration of the calcination stage. The screening of conditions to minimize belite formation indicates that calcination time should be below 1 min, at the typically high calcination temperatures required in CaL systems (i.e., slightly over 900 °C), thus ensuring that the CO_2 carrying capacity of these raw meals is kept at a level as close as possible to the value in equivalent materials with the same $CaCO_3$ content.

INTRODUCTION

The energy-intensive cement industry consumes about 2% of overall primary energy and is responsible for roughly 5−8% of global CO_2 emissions.[1,2] According to Boden et al.,[3] the emissions from the cement sector reached 2.06 $GtCO_2$ in 2014. In a situation where the demand for cement is expected to rise, CO_2 emissions from this sector could reach around 4.3 $GtCO_2$ by the year 2050.[4] About 2/3 of these emissions come from the decomposition of $CaCO_3$ present in the raw meals used to make clinker.

Several strategies have been developed in the cement industry to reduce the carbon emissions resulting from fuel combustion, such as the implementation of technical improvements for a more efficient use of the fuel, the utilization of alternative fuels (e.g., biomass or waste residues), and the use of mineral additives (e.g., fly ash, slag, etc.) to reduce clinker usage in cement production.[5] However, the CO_2 emitted from $CaCO_3$ calcination cannot be avoided with these procedures. Only CO_2 capture and storage (CCS) has the potential to drastically reduce cement CO_2 emissions,[1,4] in line with the ambitious climate change mitigation targets recently agreed at COP21 (Paris 2015).

Postcombustion calcium looping processes (CaL) have been, and continue to be, developed at the MW scale for power generation[6−9] and have also been proposed for cement plants.[10−31] Calcium looping is a technology based on the use of CaO as a regenerable sorbent of CO_2, by interconnecting a high velocity carbonator reactor with an oxy-fired calciner, in which $CaCO_3$ decomposes into CaO and CO_2.

In principle, there are two possible approaches to the use of calcium looping processes in a cement plant if the materials employed are intended for the CO_2 capture. One involves the use of standard limestone-rich materials as the main feedstock for the calcium loop. This essentially means that CaO, together with small amounts of ash and other products resulting from the combustion of fuel in the calciner, will be present in the carbonator during the CO_2 capture stage (as in the case of CaL systems developed for power plants).[32,33] As the individual components of the raw meal in a cement plant will need to be thoroughly mixed (to facilitate the slow solid−solid reactions involved in the formation of clinker in the kiln), the configuration will require a subsequent mixing (and probably also milling)[23] of the CaO-rich material purged from the calciner together with other additives needed for cement clinker (i.e., clay, marls, etc.) in order to obtain the desired elemental composition before it enters the kiln.

The second approach involves the direct use of the raw meal in the calcium loop (see Figure 1). The use of natural marls as raw meal is preferred in cement plants because the Ca−Si compounds are mixed at almost atomic level. This alternative allows the calcined solids from the calciner of the CaL system to be fed directly into the kiln.[24,34] Regarding the CaL energy balance, the presence of inert materials in the raw meal (mainly Si- and Al-based compounds) will increase the energy requirements in the calciner, since these solids will be acting as thermal ballast for the system. However, at the same time the characteristic large makeup flow of $CaCO_3$ needed in CaL systems designed for cement plants will increase the average activity of the CaO in the carbonator, thereby compensating for the energy penalty resulting from the presence of inert materials.[19,22,24,33,34]

The theoretical synergy of CaL with cement manufacture has been investigated in previous simulation works and lab scale studies.[11,13−15,17−19,21−28,30] However, hardly any experimental information on the performance of the raw meals as CO_2

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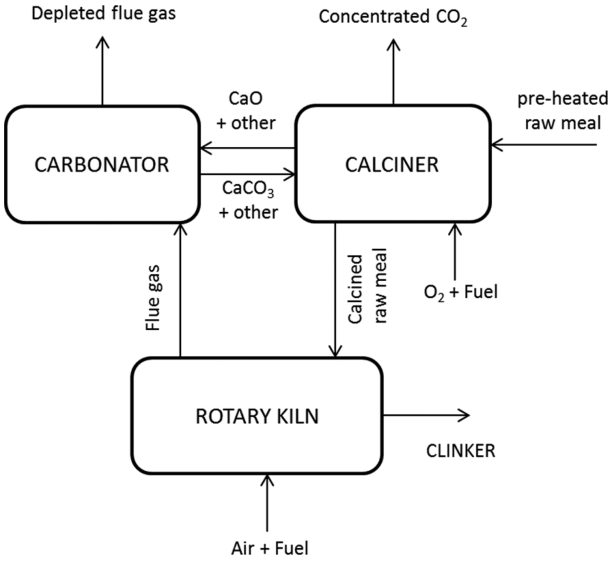

Figure 1. Schematic diagram of a calcium looping system designed for the CO_2 capture in a cement plant.

sorbents in CaL systems is available in the literature. Only Pathi et al.[21] have carried out cyclic experiments in a thermogravimetric analyzer (TGA) to study the effect of SiO_2, Al_2O_3, and Fe_2O_3 on the CO_2 carrying capacity of the CaO present in raw meals. They reported that the calcination conditions and the formation of belite (Ca_2SiO_4) affected the activity of the CaO present in the raw meals over multiple carbonation/calcination cycles.

This work investigates the suitability of several natural raw meals taken from existing cement plants as CO_2 sorbents and of a synthetic material especially tailored in our lab to have similar Ca/Si ratios to those of the raw meals. The CO_2 carrying capacity of these raw meals assuming particles of the same size as those in the cement manufacture process (i.e., particle size of around 10−20 μm on average) is examined under temperature and gas composition conditions typical of CaL systems integrated in cement plants.

EXPERIMENTAL SECTION

Materials. Three raw meals obtained from different cement plants in Spain and Italy (RM1-3) were tested, together with a "synthetic Ca−Si mixture", SM, composed of a mixture of a reference limestone ("Imeco") used in previous studies for CO_2 capture[35] and commercial SiO_2 nanoparticles. The synthetic Ca−Si mixtures were prepared by mixing 84 w/w % of the limestone with Aerosil 380 (Evonik Co., fumed silica (>99.8% SiO_2), 380 m^2/g, with a particle diameter of 7 nm). One of them (called SM-DM) was prepared in dry mode using a laboratory mixer, whereas the other (called SM-WM) was prepared in wet mode using deionized water. The prepared solution was then centrifuged and dried overnight in an oven at 110 °C.

An X-ray fluorescence spectrometer (SRS 3000 Bruker) was used to determine the chemical composition of the raw meals following the fused cast-bead method (PERLX'3 Philips). The particle size distributions were measured by a Beckman-Coulter LS 13320 laser diffraction particle size analyzer in wet mode, using ethanol as dispersant agent. The raw meals had similar chemical compositions (see Table 1) and consisted of very fine solids (dp_{max} < 170 μm and d50 between 8 and 9 μm). However, their particle size distributions presented very different shapes (see Figure 2).

Figure 2 shows that raw meals RM2 and RM3 seem to be mixtures of separate compounds, as different volumetric fractions can be clearly differentiated into distinct particle size ranges. In contrast, RM1 and the limestone used to make synthetic Ca−Si mixtures present more homogeneous particle size distributions.

Table 1. Chemical Compositions Measured by XRF

oxide (w/w%)	RM1	RM2	RM3	limestone
CaO	42.7	36.3	42.3	54.2
Al_2O_3	4.1	3.9	2.6	0.4
SiO_2	13.4	18.4	15.5	0.9
Fe_2O_3	1.9	2.2	1.6	0.4
K_2O	0.9	1.1	0.5	
MgO	0.7	1.3	0.9	0.8
MnO		0.1	0.1	
SrO			0.1	
TiO_2	0.2	0.2	0.2	
SO_3	1.0	1.4	0.2	0.1
LOI[a]	35.0	35.2	35.9	43.2

[a]Loss on ignition.

Scanning Electron Microscopy (SEM, Quanta FEG 650 microscope) equipped with an energy-dispersive X-ray (EDX) analyzer (Ametek-EDAX fitted with an Apollo X detector) was used to evaluate the level of aggregation of the Ca/Si elements in the fresh synthetic Ca−Si mixtures. The solid samples were embedded in a resin and polished. The backscattered electron (BSE) technique shows the denser compounds in a light gray color (whereas the compounds with lower density appear in dark gray), which facilitates the detection of possible changes in the chemical compositions (through changes in molecular weight) or texture (i.e., apparent density) of the samples.

As can be seen in Figure 3 left, the silica particles observed in the wet mixture (i.e., the light gray particles) are larger and have a higher apparent density than the silica particles in the dry mixture (i. e., the medium-sized dark gray particles in Figure 3 right). In both images, the $CaCO_3$ rich particles are smaller and brighter.

The SEM analyses reveal a strong tendency of the silica nanoparticles to form agglomerates several hundred microns in diameter. Another representative characteristic of this phenomenon is that, although the weight fraction of the limestone in both raw meals is the same (84 wt %), the area fraction of the limestone looks much smaller due to the large size of the silica agglomerates in the dry mixture. As a result, due to the presence of these large agglomerates, only a small level of aggregation between the limestone (white particles) and silica is observed in the dry mixture, despite the apparently small size of the individual particles of both the $CaCO_3$ and SiO_2. This situation recurs in the wet mixture, although there is a clear improvement as can be seen in Figure 3, left. The silica agglomerates are more fully covered by limestone particles. This should translate into a higher level of aggregation between the Ca and Si components and result in an increase in the rate of solid−solid reactions involved in the formation of belite, as observed below.

Experimental Setup and Methods. The reaction tests were carried out in an in-house designed thermogravimetric analyzer (TGA) that has been described in detail elsewhere.[36,37] Each sample was placed in a platinum pan that was suspended inside a mullite tube (2.54×10^{-2} m O.D.) located inside an oven that can operate at temperatures of up to 1000 °C. The reaction gases (H_2O, CO_2, air) are introduced through the base of the mullite tube at a total gas flow rate of 7.3×10^{-6} Nm^3/s. The permanent gases come from bottles, whereas the steam is produced in an in-house built generator from distilled water contained in pressurized cylinders (4 bar). The flow rate of the water is controlled by means of a Bronkhorst liquid mass flow controller. Liquid water is vaporized downstream by means of two heating tapes of 700 W. The temperature of the heating tapes is adjusted by means of a temperature controller. A continuous and steady flow of steam is generated during the test. A three-way pneumatic valve connected to the heated pipeline ensures a continuous flow of steam during the change from steam conditions to nonsteam conditions (or vice versa).

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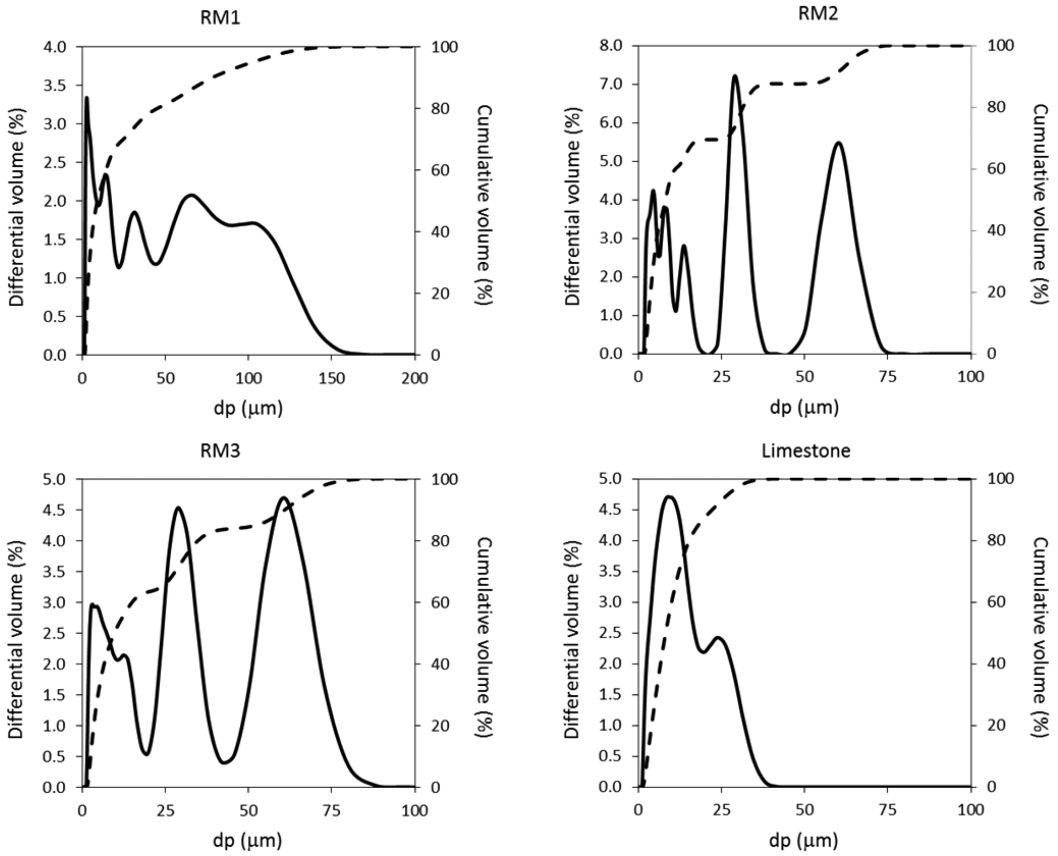

Figure 2. Particle size distributions of the three commercial raw meals and the limestone used to prepare the synthetic Ca−Si mixtures (obtained by laser diffraction).

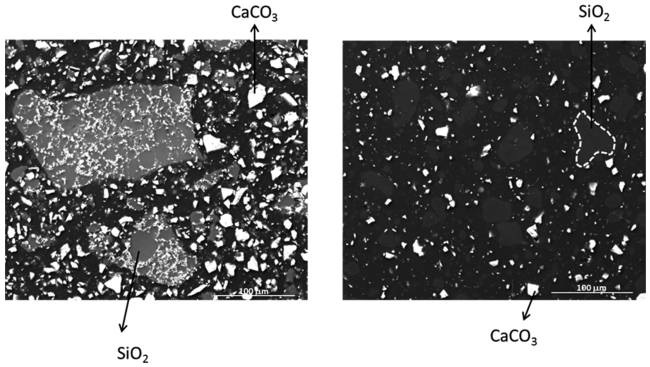

Figure 3. BSE-SEM images of the synthetic Ca−Si mixtures. Left: fresh SM (WM); right: fresh SM (DM).

The amount of sample used in the cycling tests ranged between 3 and 15 mg. The carbonation was carried out at 650 °C using 10 vol % CO_2 in air. The duration of this stage varied between 5 and 10 min depending on the initial weight of the sample. During the calcination stage, the atmosphere, temperature, and duration of the reaction were varied in order to study the influence of these parameters on the maximum carrying capacity of the raw meals.

In order to identify the main chemical species present in the CO_2 sorbents after the calcination tests, X-ray diffraction (XRD) analyses were performed using a Bruker D8 powder diffractometer equipped with a Cu Kα monochromatic X-ray tube, a Göbel mirror in the incident beam, and a parallel-slit analyzer in the diffracted beam. Diffraction data were collected by step scanning using a step size of 0.02°, a scan step time of 1 s, and a scan range of 5°−60° 2θ. For the XRD analyses, samples above 50 mg were calcined in the TGA under different conditions.

RESULTS AND DISCUSSION

The carbonation/calcination tests were first carried out at a calcination temperature of 900 °C in air for 10 min. The evolution of the carrying capacities of the raw meals and the limestone, defined as molar conversion of CaO present to $CaCO_3$, is shown in Figure 4. The decay in the carrying capacity with the number of cycles (X_N) of the CaO from limestones can be described by the equation of Grasa and Abanades[38]

$$X_N = \frac{1}{\frac{1}{(1 - X_r)} + kN} + X_r \quad (1)$$

where k is the deactivation constant, and X_r is the residual conversion. The evolution of the carrying capacity of the limestone with the number of cycles is represented by eq 1 (see continuous line in Figure 4) using the typical values reported in the literature of 0.52 and 0.075 for k and X_r, respectively.[38] However, a substantial deactivation can be observed in this plot for all the raw meals (especially in the case of the marl RM1). The shape of the curves indicates that the deactivation takes place during the first cycle. CO_2 carrying capacities between 43% and 70% lower than those of the CaO obtained from the limestone were observed. From the first cycle onward, the decay in the CO_2 carrying capacity can be represented by means of eq 1, assuming that the free moles of CaO represent no more than 60% of the total in the case of RM2 and RM3 (dashed line) and around 30% of the total in the case of RM1 (dotted line). This means that sorbent deactivation is caused by CaO sintering (as occurs in natural limestones).

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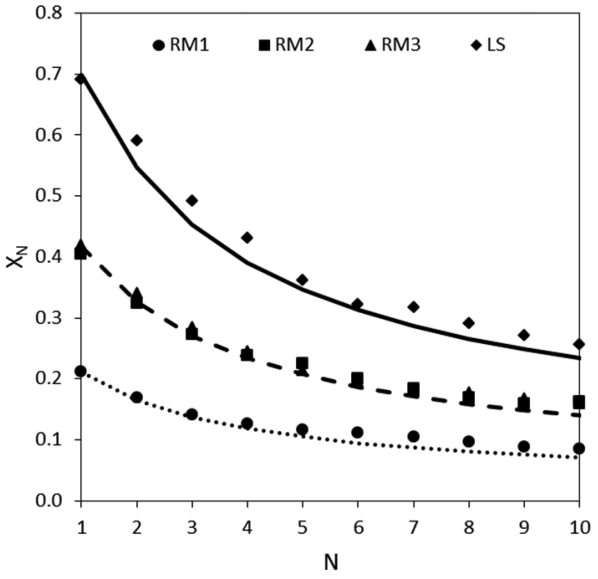

Figure 4. Evolution of the maximum conversion of CaO with the number of carbonation-calcination cycles for the three raw meals and limestone (T_{calc} = 900 °C, t_{calc} = 10 min in air, T_{carb} = 650 °C, t_{carb} = 10 min, 10 vol % CO_2 in air).

To find the cause of the great deactivation observed after the first calcination in the raw meals, samples of two raw meals calcined under different temperatures and atmospheres (i.e., air, CO_2, and steam) were analyzed by XRD.

As can be seen in Figure 5, dicalcium silicate (Ca_2SiO_4 or belite) is present in all the samples after calcination, for all the conditions tested. It is well-known that belite is an early product resulting from the calcination of calcite in the presence of quartz during the manufacture of cement.[39] Wolter[39] measured the compositions of calcined kiln inlet meals from about 20 cement plants. That study showed that at high degrees of calcination the content of free CaO in the samples ranged from 25% to 45%, whereas the amount of belite formed was between 30% and 65%, depending on the heterogeneity of the raw meal. Moreover, in a recent study, Pathi et al.[21] also observed the presence of belite in calcined samples of the raw meals by means of XRD.

The formation of belite reduces the amount of active CaO for the capture of CO_2, which explains the drop in the CO_2 carrying capacities of the raw meals observed after the first calcination step. Consequently, the influence of the calcination conditions on the carrying capacity in the first cycle of several raw meals at different Ca−Si aggregation levels was studied in detail. The most important results are explained below.

Influence of Calcination Time. Figure 6 shows the evolution of the CaO molar conversion (X_{CaO}) with time for five raw meals during a carbonation test after the first calcination stage was carried out in air at 900 °C for 10 and 1 min. As can be seen in Figure 6 (left), after 10 min of calcination the maximum molar conversion of CaO achieved during the carbonation varied between 0.2 for the natural marl (RM1) and 0.55 for the synthetic Ca−Si mixture in the dry mixture (SM-DM). The synthetic Ca−Si mixture in the wet mixture (SM-WM) achieved a molar conversion of 0.4, similar to the values of the raw meal mixtures (RM2 and RM3). These results confirm the considerable differences in behavior among the raw meals at calcination times of around 10 min, possibly due to the different levels of aggregation of Ca and Si elements in the materials. When the calcination time is shortened to about 1 min (see Figure 6 right), the CaO molar conversion during the carbonation exceeds 0.5 for the raw meals made up of mixtures of individual fine particles of $CaCO_3$ and SiO_2,

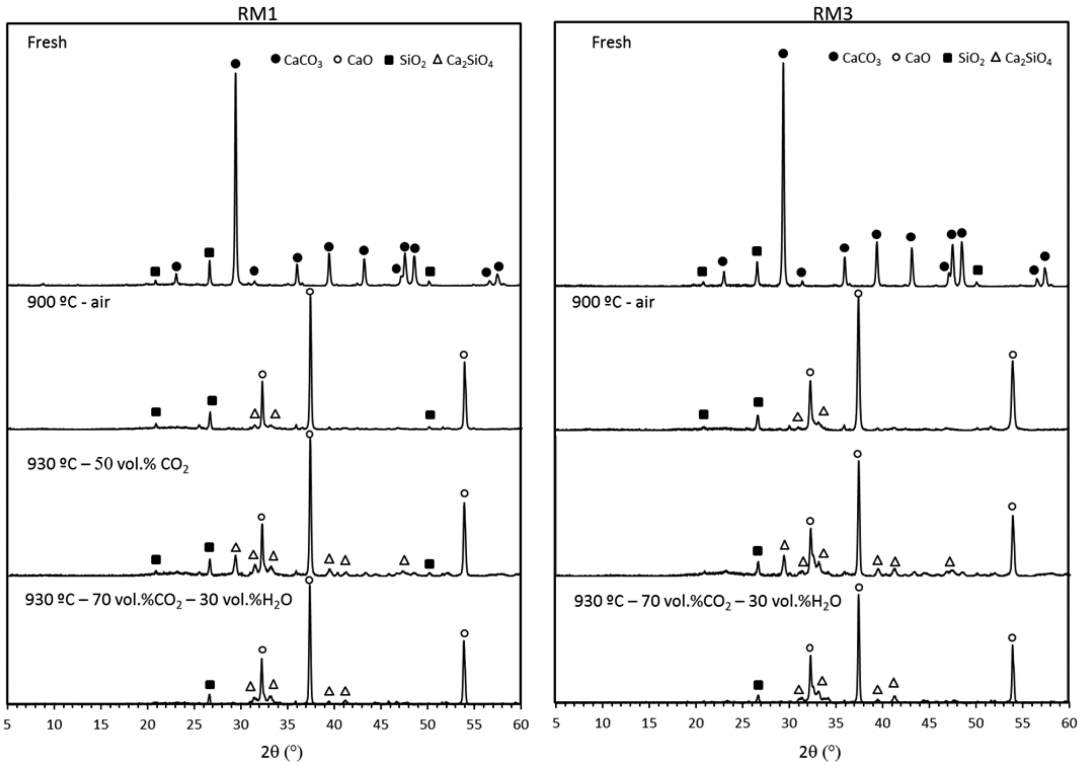

Figure 5. XRD spectra of two raw meals calcined under different temperatures and atmospheres.

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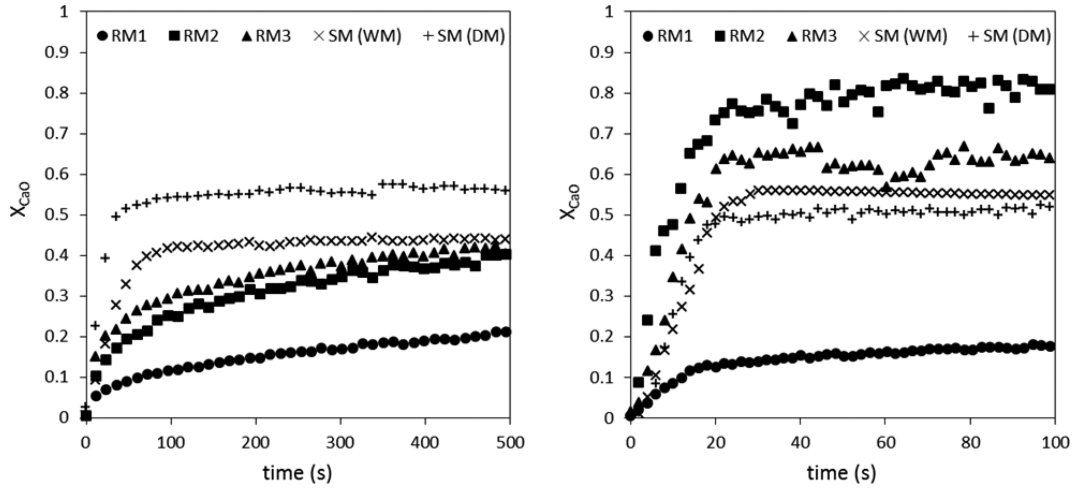

Figure 6. Effect of the calcination time on the subsequent carrying capacity during the first carbonation cycle of the three raw meals (RM1-3) and of two synthetic Ca−Si mixtures (SM). Left: calcination time 10 min. Right: calcination time 1 min (T_{calc} = 900 °C, air, T_{carb} = 650 °C, 10 vol % CO_2 in air).

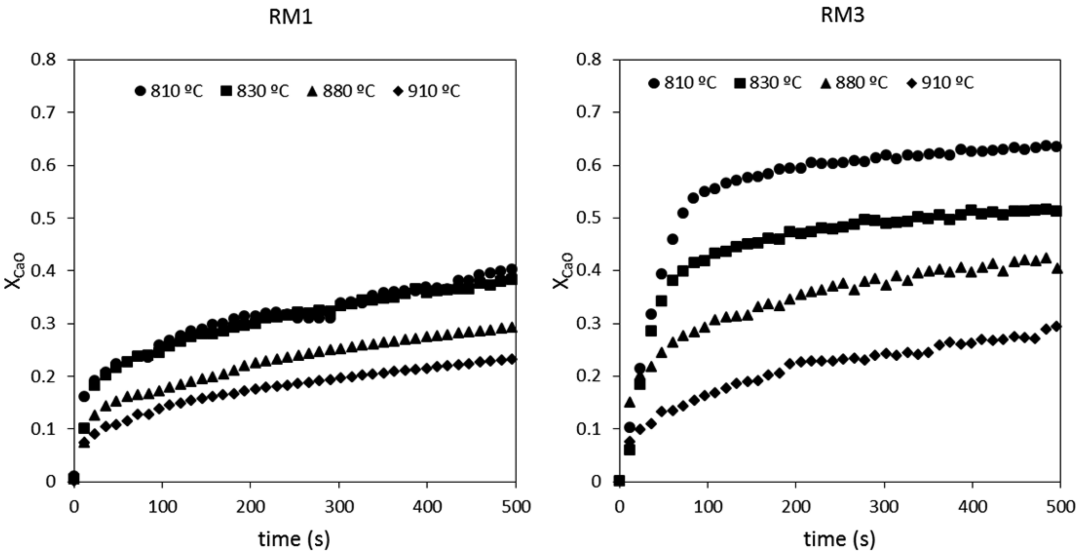

Figure 7. Effect of the calcination temperature on the subsequent carrying capacity during the first carbonation of two calcined raw meals (RM1 and RM3). Left: RM1, calcination time 1 min in air; right: RM3, calcination time 10 min in air (T_{carb} = 650 °C, 10 vol % CO_2 in air).

including the synthetic Ca−Si mixtures. This suggests a possible strategy for minimizing the deactivation caused by the formation of belite: applying flash calcination conditions (gas solid contact times in the order of a few seconds) should be able to minimize the formation of belite until sufficiently high calcination conversions are achieved. These calcination conditions and reaction times are present in large-scale commercial calciners in cement plants but cannot be reproduced on the TGA equipment of our laboratory, because the inherent heat transfer limitations around the sample pan in our TG limit the effective heating rates to below 500 K/min.

Regarding the marl-type raw meal, CaO conversions during the first carbonation are just around 0.2. This indicates a much faster belite formation rate in this sample and suggests the need for shorter calcination times to minimize the formation of belite. However, in other raw meals where Ca and Si are separated in different solid particles at micrometric scale, and as long as they are calcined for no more than 1 min, the activity of the material toward CO_2 is similar to what one would expect of a calcined solid containing the same fraction of free $CaCO_3$.

Influence of Calcination Temperature. The effect of the calcination temperature on the CO_2 carrying capacities of two raw meals (RM1 and RM3) is shown in Figure 7 for two calcination times (1 and 10 min). The calcination stage in these tests was carried out in air at different temperatures, from 810 to 910 °C. As can be seen in Figure 7, the CO_2 carrying capacities of both raw meals decreased as the calcination temperature increased. These results are in agreement with those reported by Pathi et al.[21] for other raw meals and their parent limestone.

As can be seen in Figure 7 (left), the marl-type raw meal RM1 achieved CaO molar conversions lower than 0.4 after 500 s during the carbonation test at all the calcination temperatures tested in spite of the very short calcination time (i.e., 1 min). However, a similar CaO molar conversion was attained in the artificially mixed raw meal RM3 after calcination at 880 °C for 10 min. It can be seen from Figure 7 (right) that a maximum CaO molar conversion of about 0.6 after 500 s was achieved in the raw meal RM3 after calcination at 810 °C. These results confirm that RM1 exhibits a more pronounced formation of

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belite even under very mild calcination conditions (i.e., calcination in air at 810 °C for 1 min) which can be associated with this raw meal's higher level of aggregation between Ca and Si compared to RM3. As a result, the maximum carrying capacity that the raw meal RM1 can reach is about 43% lower than what can be expected of CaO from limestone. On the other hand, the CO_2 carrying capacity of the raw meal RM3 (with a lower level of aggregation) is greatly affected by the calcination temperature. Although RM3 exhibits the CO_2 sorption capacity of CaO from a limestone after calcination at 810 °C for 10 min, CaO conversion in RM3 is about 59% lower than that of CaO from limestone calcined at 910 °C (see Figure 7 right). These results suggest that it might be preferable to use mixed raw meals (like RM3) as CO_2 sorbents for Ca looping, as the lower level of aggregation between Ca and Si would impede the formation of belite and contribute to the maintenance of higher CO_2 carrying capacities after a multicycle operation.

Influence of Calcination Atmosphere. Additional experiments in the presence of CO_2 and steam (instead of dry air) during the calcination stage were carried out as such conditions can be more representative of the atmosphere in a Ca-looping calciner. It is well-known that CO_2 and steam can promote sintering of the nascent specific surface area of CaO,[40] leading to a rapid decrease in this parameter with time. Figure 8 shows

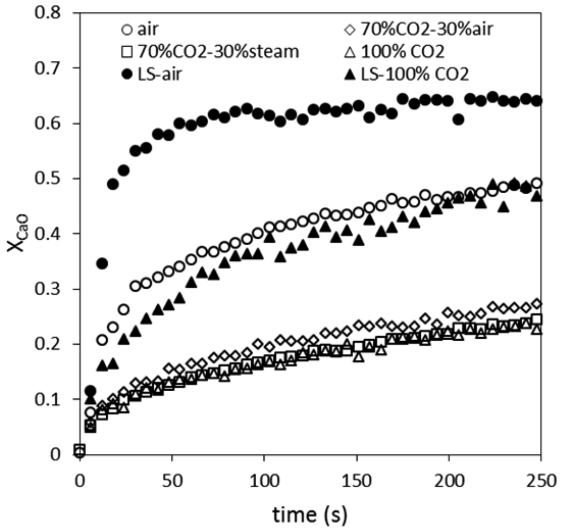

Figure 8. Effect of CO_2 and/or steam during calcination on the maximum molar conversion of CaO during the subsequent carbonation step in the raw meal RM2 (calcination carried out at 945 °C for 2 min; carbonation performed at 650 °C in 10 vol % CO_2).

a reduction of about 23% in the carrying capacity of the CaO from limestone when the calcination is carried out with 100 vol % CO_2 instead of air (see open symbols). These results indicate that the formation of belite is favored under high CO_2 concentrations, high temperatures, and calcination times of 2 min, resulting in a further decrease in the carrying capacity of the solids.

Moreover, a maximum CaO molar conversion of 0.25 was achieved by RM2 (a mixed raw meal similar to RM3) after the first calcination at 945 °C for 2 min in the presence of 70 vol % of CO_2 (and 30 vol % air), which is 50% lower than the CaO conversion achieved when calcination was performed in air conditions.

The presence of steam during calcination (70 vol % of CO_2, 30 vol % steam) did not result in any further deactivation, as the calcined raw meal achieved a CaO molar conversion only slightly lower than 0.25 after carbonation for 250 s. The drop in the carrying capacity of the solids observed due to the presence of CO_2 during the calcination might have been due to an increase in the reaction rate to form belite. These data are in close agreement with Pathi et al.[21] who also observed a drop of around 53% in the CO_2 carrying capacity of calcined raw meals with the number of cycles when the calcination stage was carried out in the presence of CO_2. As a high concentration of CO_2 in the calciner is unavoidable during the sorbent regeneration stage in a CaL system, an attempt to reduce the calcination time to only 30 s was made, while at the same time maintaining a high calcination temperature of 930 °C and a reaction atmosphere with 70 vol % CO_2 and 30 vol % steam. The evolution with time of the conversion of CaO from raw meals, limestone, and synthetic mixtures during the subsequent carbonation stage is represented in Figure 9. When the

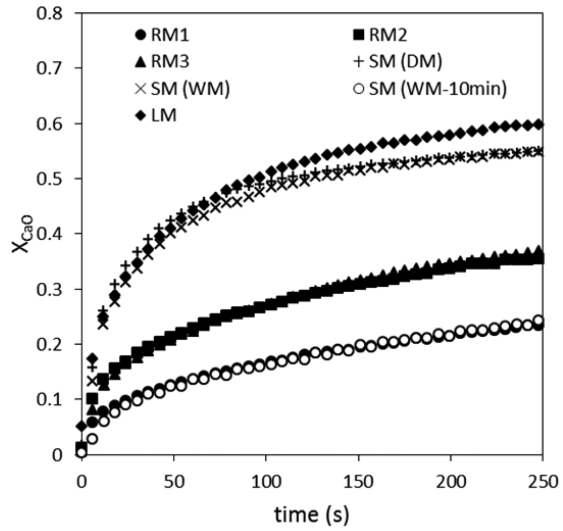

Figure 9. Evolution of the CaO molar conversion during the carbonation of the raw meals, limestone, and synthetic mixtures after calcination carried out in 70 vol % CO_2 and 30 vol % steam at 930 °C for 30 s. For comparison, also the SRM (VM-10 min) results with 10 min calcination at the same conditions are plotted.

calcination time was reduced to 30 s, the synthetic Ca−Si mixtures (SM), that showed a lower level of Ca−Si aggregation, achieved a maximum molar conversion of 0.5 after 250 s, which is only slightly lower than that attained by CaO from limestone. Under the same conditions, the marl-type raw meal (RM1) only achieved a CaO molar conversion of about 0.3 (i.e., around 60% lower than the value achieved by CaO from limestone), which matches the value achieved by the synthetic Ca−Si mixture (SM-WM) when the calcination time was increased to 10 min (white circles in Figure 9). The mixed raw meals (RM2 and RM3) showed a behavior in-between that of the synthetic and that of the marl-type materials.

The results confirm that raw meals can be used as precursors of CO_2 sorbents for CaL systems integrated with cement plants, but their behavior as CO_2 sorbents differs greatly depending on the origin of the raw meal and the calcination conditions. The level of aggregation between the Ca and Si compounds will have a strong influence on the maximum carrying capacity of the sorbents after the first calcination cycle.

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In order to maximize the performance of a CaL system operating in a cement plant, it would be preferable to use a mixed raw meal rather than a marl-type raw meal. The calcination time should be reduced as much as possible (to less than 1 min) in order to minimize the formation of belite and achieve the maximum possible activity of the CaO toward CO_2.

CONCLUSIONS

In this work, the ability of commercial and synthetic Ca−Si mixtures to act as CO_2 sorbents in cement plants has been studied. The calcination of the raw meals at temperatures higher than 900 °C in CO_2 rich atmospheres (which are typical conditions of Ca looping systems) favors the formation of belite, which can deactivate a substantial fraction of the CaO present in the raw meals. The level of aggregation between Ca and Si compounds in the raw meals has a strong effect on the formation of belite. In marl-type materials, where there is a higher level of aggregation, the formation of belite is greatly favored, and therefore, these raw meals undergo greater deactivation with the number of cycles, with CO_2 carrying capacities falling to below 0.2. However, the CaL operation with these materials would still be possible with larger solids circulation rates to compensate for the lower activities. In contrast, the use of mixed raw meals (i.e., particles of SiO_2 and $CaCO_3$ separated at micrometric scale) hampers the formation of belite, making these materials more suitable for the CO_2 capture, particularly with calcination times of less than 1 min.

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Notes

The authors declare no competing financial interest.

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